Appl.No. 09/863,558
Attorney Docket 124172-1026 (D#81,564-D1)

THE UNITED STATES PATENT AND TRADEMARK OFFICE

Serial No.: 09/863,558 **Art Unit:** 1626

Applicants: CLEMENTS et al. **Examiner:** E.O. SACKEY

Filed: May 23, 2001

Title: Preparation Of Hydroxyalkylcarbamates From Six-Membered Cyclic Carbamates

Rule 1.132 Declaration Of John Clements

I JOHN H. CLEMENTS, the undersigned, state the following:

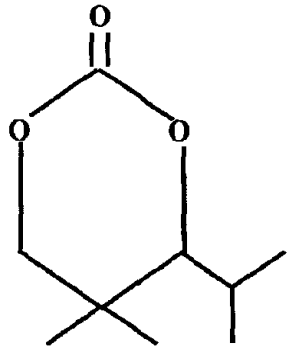
1. I received a Bachelor of Science Degree in Chemistry from the University of South Carolina in Columbia, South Carolina. I received the degree of Doctor of Philosophy in Chemistry from the University of Texas in Austin, Texas.

2. I have been employed by Huntsman Petrochemical Corporation in Austin, Texas, since 1999, and have been engaged in research in the field of organic chemistry. More specifically, I have been engaged in a research program directed to coatings applications.

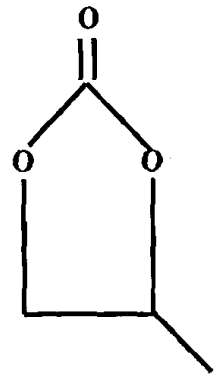
3. In response to a request by the U.S. Patent Office made in connection with the above-identified patent application, two long-term stability tests were conducted to determine and compare the stability of hydroxyalkylcarbamate compounds synthesized from 6-membered and 5-membered cyclic carbonate compounds. These tests were conducted on or about March 27, 2003 to April 23, 2003 and on or about May 5, 2003 to June 5, 2003.

4. The 6-membered and 5-membered cyclic carbonate compounds used in synthesizing the hydroxyalkylcarbamate compounds for these tests had the following structures:

Cyclic Carbonate I: XHC-30 Carbonate (a 6-membered cyclic carbonate; Huntsman Performance Products; having a formal name: 4-isopropyl-5,5-dimethyl-1,3-dioxolan-2-one)



Cyclic Carbonate II: Propylene Carbonate (a 5-membered cyclic carbonate)



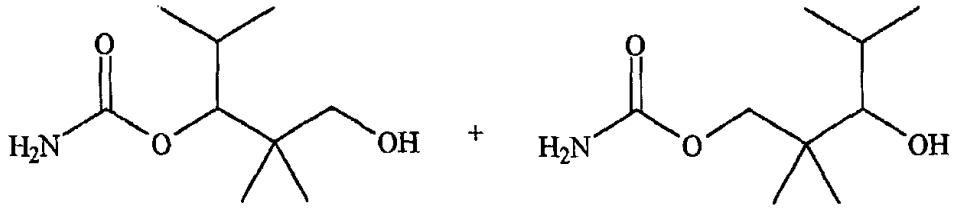
5. The following hydroxyalkylcarbamate compound, Hydroxyalkylcarbamate I, was synthesized from the reaction of 6-membered Cyclic Carbonate I with ammonia (NH_3):

Hydroxyalkylcarbamate I: $C_9H_{19}NO_3$

6. The following hydroxyalkylcarbamate compound, Hydroxyalkylcarbamate II, was synthesized from the reaction of 5-membered Cyclic Carbonate II with ammonia (NH_3):

Hydroxyalkylcarbamate II: $C_4H_9NO_3$

7. Hydroxyalkylcarbamate I was synthesized according to the following procedure: 398g of Cyclic Carbonate I (synthesized from 2,2,4-trimethyl-1,3-pentanediol and dimethylcarbonate, purity 98.7% basis GC area %) was placed in a clean and dry 1-liter autoclave. The vessel was then sealed and purged with nitrogen for 45 minutes. During this time, the reactor contents were warmed to 40°C with stirring. 50g of ammonia (29% excess) was metered into the vessel and the resulting mixture heated to 70°C over the course of 1.5 hours. The contents were then held at 70°C and allowed to react for an additional 1.5 hours. The resulting product was cooled to 40°C and discharged. A low-color product was obtained that froze shortly afterward to a white solid. The white solid product was spread over the surface of a shallow glass container and excess ammonia removed under a vacuum of 5 mmHg for 4 hours at 55°C. During this time, the product melted. Once cooled, a solid white powder with no odor of trace ammonia was obtained. This solid white powder corresponds to an 85/15 (mole ratio) mixture of Hydroxyalkylcarbamate I Isomers A and B (illustrated below) as observed by CNMR analysis:



Isomer A + Isomer B

Hydroxyalkylcarbamate I was then analytically tested, and determined to be sufficiently pure No unreacted Cyclic Carbonate I or 2,2,4-trimethyl-1,3-pentanediol (TMPD); the primary impurity in Cyclic Carbonate I, was detected by CNMR analysis. Additional analysis of Hydroxyalklycarbamate I was as follows:

Melting point = 65°C
Total amine = 0.0118 (corresponds to < 0.03% unreacted ammonia)
0.25 wt. % TMPD as detected by HPLC analysis.

Hydroxyalkylcarbamate II used in this study was obtained commercially from Huntsman under the trade name CARBALINK® hydroxylpropyl carbamate (HPC). Hydroxyalkylcarbamate II conformed to all sales specifications for this product.

8. A long-term stability test for Hydroxyalkylcarbamates I and II was then conducted in a temperature-controlled oven. During the long-term stability test, Hydroxyalkylcarbamates I and II were exposed to a temperature of 80°C for 86.5 hours.

9. Samples of Hydroxyalkylcarbamates I and II were taken at various times throughout the long-term stability test. The samples were analytically tested, and the results observed and recorded in Table A as set out immediately below:

Table A

Hydroxy-alkyl-carbamate	Time (hrs)	Total Amine (meq/g)	2+3 Amine (meq/g)	Wt. % NH_3	Wt. % By-product	Wt. % Cyclic Carbonate	Wt. % Glycol
I	0	0.0118	~0	0.02	~0	~0	0.25
I	19	0.0080	~0	0.01	~0	~0	0.12
I	39.5	0.0010	~0	~0	~0	~0	0.44
I	86.5	~0	~0	~0	~0	~0	0.27
II	0	0.2537	0.2321	0.04	~0	1.08	0.34
II	19	0.5059	0.0437	0.79	~0	2.33	2.37
II	36.5	0.4674	0.0230	0.76	~0	1.84	2.87
II	86.5	0.3602	0.0114	0.59	~0	7.66	4.46

Due to difficulty in measuring the amount of Cyclic Carbonate I in samples of Hydroxylalkylcarbamate I via the HPLC method employed to generate the above data, CMNR analysis was also performed on the Hydroxyalklycarbamate I sample exposed to 80°C for 86.5 hours. The results of this analysis indicated a 0.2/84.5/15.3 molar ratio of Cyclic Carbonate I to Hydroxyalkylcarbamate I Isomer A to Hydroxyalkylcarbamate I Isomer B. This corresponds to a 0.18 wt. % level of Cyclic Carbonate I. Additional species were not detected. Note that little change in the ratio of isomers A and B was observed as compared to the ratio at the beginning of the long-term stability test, thus confirming the structure of Hydroxyalkylcarbamate I.

Information provided in Table A is defined as follows:

a) Hydroxyalkylcarbamate refers to Hydroxyalkylcarbamate I or II.
b) Time refers to the time the hydroxyalkylcarbamate sample was taken during the long-term stability test, recorded in hours (hrs).
c) Total Amine refers to the total amount of amine present in the sample, recorded in milliequivalents/gram (meq/g).
d) 2+3 Amine refers to the amount of secondary and/or tertiary amine present in the sample, recorded in milliequivalents/gram (meq/g).
e) Wt% NH_3 refers to the weight percent of ammonia or present in the sample.
f) Wt% By-product refers to the weight percent of hydroxyalkylamine alkoxylation byproduct present in the sample (no evidence of this byproduct was observed for either Hydroxyalkylcarbamate I or II).
g) Wt% Cyclic Carbonate refers to the weight percent of Cyclic Carbonate I (XHC-30) or II (propylene carbonate), used in producing the Hydroxyalkylcarbamate, present in the sample.
h) Wt% Glycol refers to the weight percent of glycol (TMPD or 1,2 proplyene glycol) present in the sample.

The following four criteria were used to determine long-term stability: (1) Wt% Ammonia; (2) Wt% By-product; (3) Wt % Cyclic Carbonate; and (4) Wt% Glycol.

10. Based on the results, Hydroxyalkylcarbamate I, synthesized from a 6-membered cyclic carbonate, has greater long-term stability than Hydroxyalkylcarbamate II, prepared from a 5-membered cyclic carbonate. The long-term stability of Hydroxyalkylcarbamate I is evidenced by the constant amount of ammonia, cyclic carbonate and glycol as measured over time. For 86.5 hours, the weight percent of ammonia (~0 to 0.02%) and cyclic carbonate (~0%) did not change significantly. Furthermore, there was no significant change in the weight percent of glycol (0.25% to 0.44%).

11. On the other hand, the instability of Hydroxyalkylcarbamate II, prepared from a 5-membered cyclic carbonate, had increased amounts of ammonia, cyclic carbonate and glycol. The weight percent of ammonia initially increased from 0.04% to 0.79% and then leveled off to about 0.59% after 86.5 hours. Moreover, the weight percent of cyclic carbonate increased from 1.08% to 7.66%. Finally, the weight percent of glycol continuously increased from 0.34% to 4.46%.

During the long-term stability testing, the molten samples were allowed to stand in glass jars with lids slightly loosened to avoid possible pressure buildup. Under these circumstances, release of ammonia to the atmosphere can take place. Therefore, analysis of ammonia level alone is not a sufficient gauge of product quality. Only when taken together with the additional analysis performed is an accurate gauge of product quality obtained. Moreover, testing performed in containers sealed throughout the duration of the experiment may yield different results. Under these circumstances, it's theorized that the inability of liberated ammonia to escape from the container suppresses product decomposition. To test this theory, Hydroxyalkylcarbamate II was exposed to temperatures of 50°C and 60°C for 26 days in glass jars with slightly loosened lids and also in sealed stainless steel pressure bombs. The results are as follows immediately below in Table B:

Table B

Container type	Temp (°C)	Final pressure (psig)	Wt. % NH_3	Wt. % Cyclic Carbonate II	Wt. % Glycol
Jar	50	-	0.02	6.66	1.38
Jar	60	-	0.48	2.91	3.33
Pressure Bomb	50	2	0.53	2.13	1.52
Pressure Bomb	60	9	0.66	2.41	2.18

As set out in the Table B, the level of ammonia found in Hydroxyalkylcarbamate II, when exposed to temperatures of 50° and 60°C in sealed vessels (Pressure Bomb), is higher than in jars with loosened lids (Jar) owing to the inability of liberated ammonia to escape. However, the material in the sealed vessels (Pressure Bomb) has not undergone decomposition to the same extent as that in the jars based on carbonate and glycol levels.

12. Another long-term stability test had been conducted with unsuccessful protocol. In this test, a comparison of long-term stability could not be determined because of the low temperature range used. The test temperature range used in that initial test was between 60° to 70°C.

13. This other test also used a different method of synthesis. Here, hydroxyalkylcarbamate compounds were synthesized by the reaction of Cyclic Carbonates I and II with ethylhexylamine (EHA). The 6-membered Cyclic Carbonate I synthesized with EHA produced Hydroxyalkylcarbamate III ($C_{17}H_{34}NO_3$). Similarly, the 5-membered Cyclic Carbonate II was synthesized with EHA to yield Hydroxyalkylcarbamate IV ($C_{12}H_{25}NO_3$). Hydroxyalkylcarbamates III and IV were then heated, but only to a lower temperature of range 60° to 70°C for 688.5 hours. Samples of Hydroxyalkylcarbamates III and IV were taken at various times throughout this long-term stability test. The samples taken were analytically tested and the results are set out below in Table C:

Table C

Hydroxy-alkyl-carbamate	Time (hrs)	Total Amine (meq/g)	2+3 Amine (meq/g)	Wt. % EHA	Wt. % By-product	Wt. % Cyclic Carbonate	Wt. % Glycol
III	0	0.1898	~0	2.45	~0	0.90	~0
III	163.5	0.0516	0.0478	0.05	1.23	~0	0.14
III	360.0	0.0363	0.0337	0.03	0.87	~0	0.13
III	497.0	0.0317	0.0295	0.03	0.76	~0	~0
III	688.5	0.0272	0.0250	0.03	0.64	~0	~0
IV	0	0.1531	~0	1.98	~0	~0	~0
IV	163.5	0.0499	0.0467	0.04	0.87	0.11	0.13
IV	360.0	0.0393	0.0357	0.05	0.67	0.06	0.22
IV	497.0	0.0367	0.0341	0.03	0.64	0.10	0.09
IV	688.5	0.0402	0.0402	0.04	0.69	0.11	0.12

14. The protocol for determining the long-term stability of Hydroxyalkylcarbamates III and IV was ineffective at temperatures of 60°-70°C in demonstrating differences in ethylhexylamine, by-product, cyclic carbonate or glycol over time.

15. The test data presented in Table A (as contrasted with Table C) clearly demonstrate the following facts:

(1) Hydroxyalkylcarbamate I, produced by the reaction of a 6-membered cyclic carbonate and ammonia, displays stability over time, based on the constant amount of ammonia, cyclic carbonate and glycol observed and recorded over time;

(2) Hydroxyalkylcarbamate II, produced by the reaction of a 5-membered cyclic carbonate and ammonia, displays instability over time, based on the increased amount of ammonia, cyclic carbonate and glycol observed and recorded over time; and

(3) the protocol used in determining the long term stability of Hydroxyalkylcarbamates III and IV, produced by the reaction of 6 and 5-membered cyclic carbonates with ethylhexylamine, respectively, was ineffective at the reduced test temperatures.

I declare that all statements made of my own knowledge are true, and that all statements made on information and belief are believed to be true. I made these statements with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and may jeopardize the validity of the application or any patent issued thereon.

John H. Clements